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The inventor has requested not to be named

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Process for the preparation of acyl derivatives of the enol form
of codeinone

Patented in the Federal Republic of Germany on July 17, 1951

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It is known that the codeine by Oxidation for example, with chromic acid as well as its available codeinone Enolmethyläther that thebaine, called

Morpholspaltung suffers from: it is boiling with acetic anhydride in a neutral column piece, 3-methoxy-4,6 -diacetoxyphenanthren and Äthanolmethylamin split (L. Knorr, reports the German Chem. Society, Vol 36, S.3081 [1903]).

It has now been found that in this reaction a base, an intermediate in the cleavage reaction is obviously yield can thus make good in that one long period of acetic anhydride at room temperature or slightly elevated temperature to influence the leaves codeinone. A modification of the method is that one action of acetic anhydride at the boiling point or close to the pauses before the Morpholspaltung markedly. The workup can be done by that one Reaktionslösung to decompose the excess anhydride on a soda-ice mixture and pour the remote shakes up the base with organic solvents. Or is evaporated reaction mixture at low temperature in a vacuum which, the residue in water and making alkaline with bicarbonate. The remote base is shaken out with ether and after evaporation of the ether in crystalline form from F. = 133 to 134° obtained.

Calculated for C₂₀H₂₁O₄N: C 70.75%, H 6.24%;

found: C 70.62%, H 6.29%.

The analysis shows that the acetyl group has a codeinone added. The new compound with concentrated acids are quantitatively the same as the tieforangerote Halochromism thebaine. It has therefore a KDnstitution Enolacetats the formula

The new connection is the same reactions of the conjugated system of double bonds are subjected including thebaine is accessible. So they stored Ran double bonds anlagerungsfähige compounds such as hydroquinone or maleic anhydride to such, and with hydrogen peroxide it is oxidized to Oxycodeinon.

In the inventive implementation of acetic anhydride to liquid anhydrides of other lower fatty acids are used to place, and we obtain the corresponding acyl compounds.

Example

3 g Codeinone from F. = 180-181° to 15 g of freshly distilled acetic anhydride two days at room temperature with shaking, with the first solution is suspended in codeinone. It is evaporated under vacuum at room temperature, the excess acetic anhydride and rubs off on the resinous residue with anhydrous ether, and the acetate of Codeinonenolacetats as microcrystalline, brownish color tinged, slightly aspirated powder separates. Recrystallization from ethyl acetate gives the acetate as colorless crystals from F = 104-105°.

The acetate is dissolved in a little ice-cold water, the solution mixed with bicarbonate and secluded base with much peroxydfreiem ether was added to, with a small amount of amorphous flakes remains unresolved. Dry the ether over sodium sulfate, mixed with a little charcoal, filtered, and evaporate the ether solution on a dem Wasserbad. The resin is Codeinonenolacetat back as the time to radiate some crystals solidifies. Yield 1.9 g. Recrystallization from hexane, in which a small portion of the crude product is insoluble, is the base with a sharp melting point 133-134 receive. By the same temperature melting at Acetylcodein gives the connection is a strong point depression.

The new compound shows such as thebaine intensive Halochromism with concentrated sulfuric acid and concentrated hydrochloric acid. The picrate of the base is by releasing the same dilute acetic acid and precipitation with aqueous picric acid in procedure. The initially amorphous precipitated picrate is extracted, and at room temperature in methanol solution dried, the on concentration under vacuum initially amorphous fractions drop out, sucked is that of. Upon further concentration of the methanol solution crystallizes the picrate Codeinonenolacetats out of the twice recrystallized by after concentration the room temperature in methanol solution in prisms prepared from the F. = 201-203° under decomposition will be. With the 197° with decomposition at melting Codeinonpikrat there is a strong decrease in melting point 184-188°.

Analysis: C₂₀H₂₁O₄N · C₆H₃O₇N₃ (568.5).

Calculated: C 54.90%, H 4.25%, N 9.85%;

found: C 54.76%, H 4.23%, N 9.77%.

The picrate is in contrast to intense orange-red Codeinonpikrat Halochromism with concentrated sulfuric acid and concentrated hydrochloric acid.

Claims:

1. Process for the preparation of acyl derivatives of the enol form of codeinone, characterized in that one codeinone with liquid carboxylic, especially those of low molecular weight fatty acids, treated at room temperature.
2. Amendment of the process according to claim 1, characterized in that one anhydrides in the heat which can act on codeinone and the reaction stops before the so-called Morpholspaltung has increased noticeably.